

Stable isotopic studies on the origin of magnesite deposits in the Setogawa Group, Shizuoka, central Japan(MEMORIAL VOLUME TO THE LATE PROFESSOR TERUHIKO SAMESHIMA)

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Stable isotopic studies on the origin of magnesite deposits in the Setogawa Group, Shizuoka, central Japan

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Abstract Massive magnesite deposits in the Setogawa Group in Shizuoka were formed by an extensive carbonation of serpentinite in an ancient accretionary prism. Stable isotopic investigations of the origin of massive magnesite deposits revealed that a homogeneous deep-seated magmatic carbon mixing with marine limestones may be the main source of the carbon. Many calcite and dolomite veins occur in the serpentines, basaltic and pelitic rocks and based upon carbon and oxygen isotopes are supposed to be of similar origin to carbonate veins found in modern serpentinite diapirs of the Izu-Bonin and Mariana island arc. In contrast, massive magnesite deposits were formed during the subduction of an active volcano and/or an active ridge, with circulation of magmatic carbon providing the carbon source for the serpentinite diapirs.

Key words: carbon and oxygen isotopes, magnesite, serpentinite, Setogawa Group

INTRODUCTION

Magnesite deposits in the Setogawa group, Shizuoka Prefecture, central Japan, are located within ultramafic bodies occurring along the Sasayama tectonic line (Fig. 1). "Magnesite deposit" is a term applied in this paper to rocks formed as a result of alteration of serpentinite or mafic rocks by CO₂-bearing fluid. It is composed principally of magnesite, talc and silica minerals such as quartz and chalcedony. Kimitake-zawa and Ohtake magnesite deposits are found as large monomineralic deposits in the Setogawa serpentinite sequences which are bounded on the west by the Mesozoic Mikura Formation of the Shimanto Terrain (Sugiyama & Shimokawa 1981). Geological, mineralogical and petrological studies of these deposits were reported by Sameshima (1970ms), Takasawa & Kuroda (1974) and Ohashi (1982).

Carbon and oxygen isotopic ratios of the magnesite and other carbonates provide an excellent tool for determining the origin of the carbonic species in the ore forming fluid and estimating the formation temperature of these carbonate mineral deposits. Morteani *et al.* (1983), Jedrysek & Halas (1990), and Fallick *et al.* (1991) dis-

cussed the origin of such magnesite deposits in various settings. However, they did not refer to the magnesite deposits which were formed by replacement of serpentinite bodies by hydrothermal fluid such as from the subduction slab at convergent plate boundaries.

Recently a new type of modern serpentinite diapir was discovered in the Mariana and Izu-Bonin arc system (Fryer 1992; Fujioka *et al.* 1993). Although the nature of such serpentinite diapirs remains unclear, the serpentinites in the ancient accretionary prism of the Setogawa and Sanbagawa terrains, Japan, were suspected to have formed in the same manner as these modern serpentinite diapirs. Sameshima (1970ms) pointed out that serpentinites occur in Mineoka at Chiba Prefecture and Miura Peninsula in Kanagawa Prefecture as well as the Setogawa Group. These serpentinite complexes of the Oligocene-Miocene make a circum-Izu serpentinite zone and are thought to reflect a fossil transcurrent plate boundary (Arai, this volume).

The purpose of the present study is to clarify the origin of the magnesite deposit in the Setogawa Group by means of chemical and isotopic analyses. Also we discuss the relationship between modern serpentinite diapirs and ancient car-

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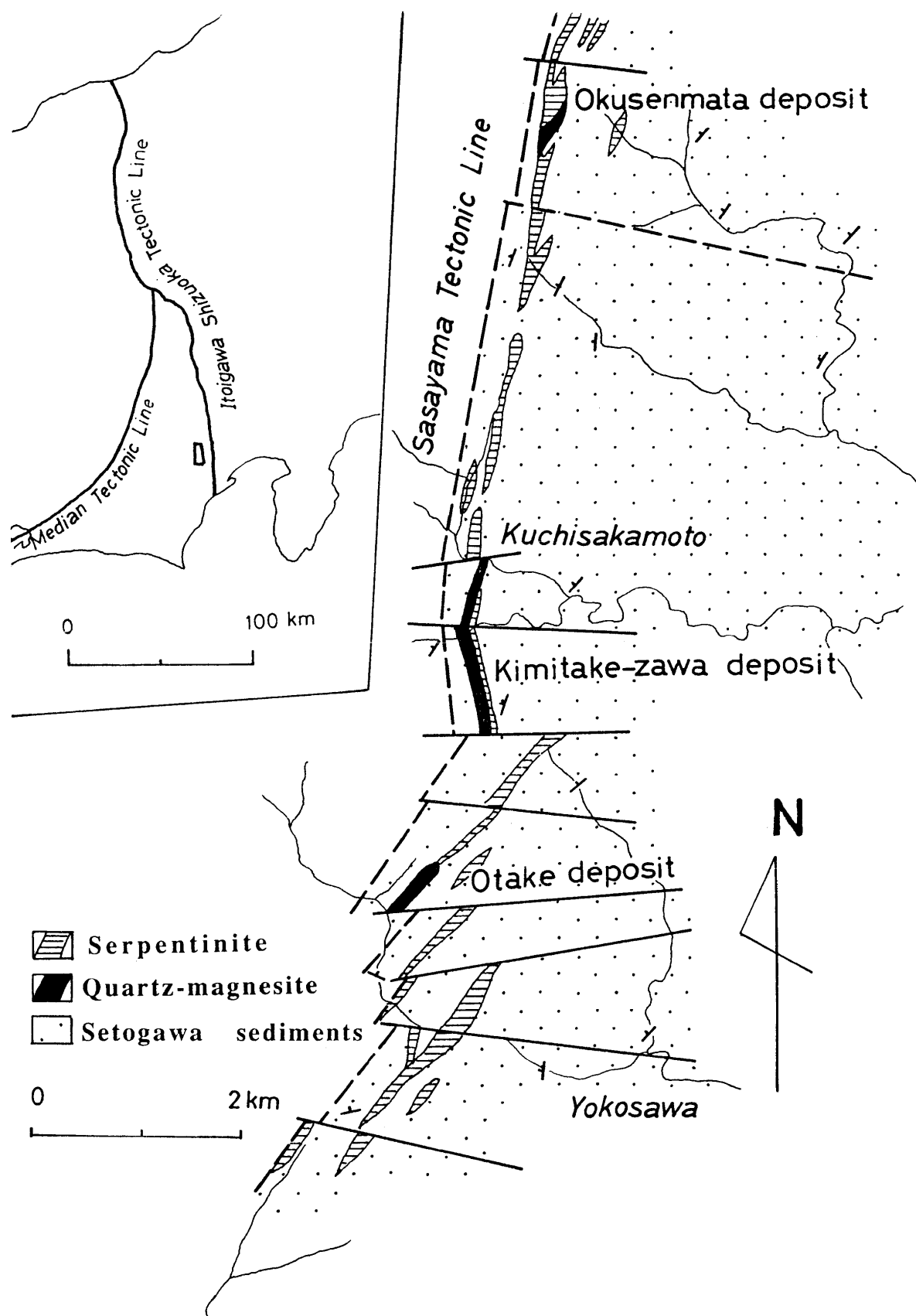


Fig. 1 Locality map of the Kimitake-zawa magnensite deposits and other serpentinites occurring in the Setogawa Group, Shizuoka Prefecture, central Japan.

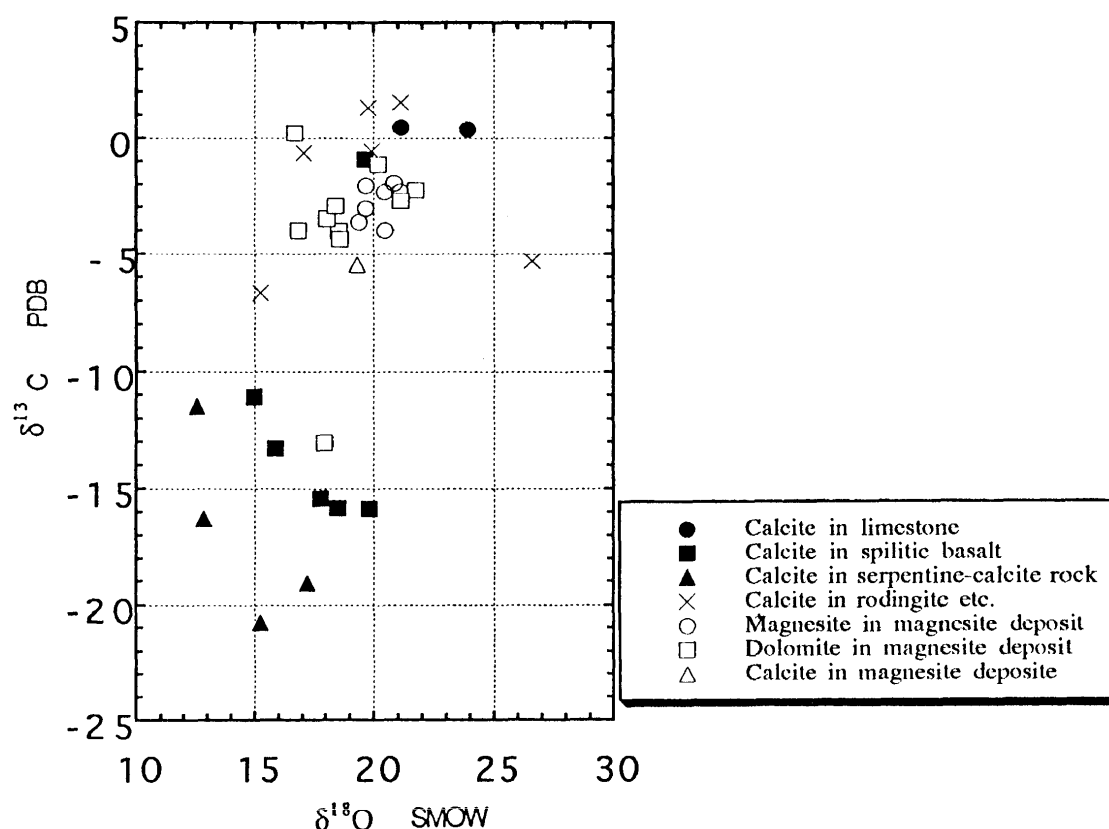


Fig. 2 Carbon and oxygen isotopic ratios of magnesite, dolomite, and calcite collected in and around the Kimitake-zawa magnesite deposits in the Setogawa Group, Shizuoka Prefecture, central Japan.

bonated serpentinite rocks in accretionary prisms.

GEOLOGY AND MINERALOGY OF MAGNESITE DEPOSITS OF THE SETOGAWA GROUP

The Kimitake-zawa magnesite deposit outcrops in the upper part of the Kimitake-zawa river (Fig. 1). The carbonated serpentinites are always oriented subparallel to the strike of the other members of the deposits, which include tectonic breccia, black shale and tuffaceous beds that are also extensively carbonated. Intense carbonatization of these rocks is especially prominent in an area that has been subjected to widespread faulting, where entire fracture zone attains a maximum thickness of more than 170 m.

Three main types of magnesite deposits can be distinguished in the carbonated serpentinites: 1) serpentine-magnesite, 2) talc-magnesite, and 3) quartz-magnesite. The serpentine-magnesite occurs mostly as brownish-yellow colored massive bodies surrounded by faults. Some of the serpentine appears to be bleached, and in thin section this lighter colouration is observed to result from the

presence of magnesite. Especially in quartz-magnesite rock, bright green filmy veins are observed which is described as Ni-bearing fuchsite by Takasawa & Kuroda (1974). Ohashi (1982) reported that serpentinite may be derived from harzburgite retaining a porphyritic appearance resulting from the selective replacement of the bastitic pseudomorph after orthopyroxene in the mesh serpentine crystals. The talc-magnesite rocks are generally restricted to narrow zones at the margins of quartz-magnesite bodies, forming a transitional zone between the serpentine- and the quartz-magnesite rocks (Ohashi 1982). The quartz-magnesite rock varies widely in appearance. Carbonate-rich parts resemble fine-grained marble, with irregular fractures. The quartz-rich rocks are chert-like; they are hard and display smooth conchoidal fracture.

As pointed out by Ohashi (1982), these three types of magnesite deposits each have their own distinctive chemical characteristics. For the serpentine-magnesite rocks, magnesite has a considerably higher and narrower range of Mg# of 92-96 {Mg/(Mg+Fe) ratio in magnesite} than the other two. In quartz-magnesite rocks, magnesites

Table 1 Sample descriptions and carbon and oxygen isotopic values of massive magnesite, dolomite and calcite of the Kimitake-zawa magnesite deposits. Abbreviations in table are as follows: chl: chlorite; chrm: chromite; dol: dolomite; ill: illite; mag: magnesite; qtz: quartz.

Sample No.	carbonate mineralogy	source rock	major constituents	$\delta^{13}\text{C}(\text{PDB})$	$\delta^{18}\text{O}(\text{SMOW})$ corrected
7080404	magnesite	serpentinite	mag-serp.	-4.00	20.47
7080403	magnesite	seperitinite	mag-talc-serp	-3.06	19.66
7080403	magnesite		monomineralic vein	-2.29	21.09
7080403	magnesite	serpentinite	mag-dol-talc-serp	-3.63	19.4
7091503	magnesite	seperitinite	mag-talc	-2.33	20.46
7091301	magnesite	serpentinite	mag-dol-qtz	-2.06	19.68
701215an	magnesite	seperitinite	mag-dolo-qtz	-1.95	20.83
7091501	dolomite	chromitite	mag-dol-qtz-chrm	-2.26	21.73
71328aob	dolomite	serpentinite	mag-dol-qtz	-2.72	21.11
701215chr	calcite	chromitite	cal-serp-chrm	-5.47	19.31
701215ya	magnesite	basic rock	mag-dol-qtz-chl	-2.84	20.58
70613no6	dolomite	basic tuff	mag-dol-qtz-chl	-4.04	18.54
70613no6	dolomite		monomineralic vein	-3.51	18.05
7181004	dolomite	basic tuff	mag-dol-qtz-chl	-13.03	17.93
7181004	dolomite	basic tuff	monomineralic vein	0.22	16.68
7061210	dolomite	basic tuff	mag-dol-qtz-chl	-4.37	18.59
7061305	dolomite	basic fuff	mag-dol-qtz-chl	-1.13	20.2
70804p-4	dolomite	shale	mag-dol-qtz-ill	-2.94	18.42
7180303d	dolomite	shale	mag-dol-qtz-ill	-4.00	16.84

mostly showed a low Mg# of 85-89. The talc-magnesite rock is intermediate in Mg# between the serpentine-magnesite and quartz-magnesite rocks.

The tectonic breccia, black shale and tuffaceous beds are variably carbonated. Most of the carbonated shales contain two types of carbonates, ferroan magnesite and dolomite. The carbonated basic tuff is variable in texture and often shows many small vugs filled with calcite and chlorite. Fine grained dolomite and magnesian calcite in basic tuff, fill the smaller cavities and form an encrustation in the vugs. Calcites from rodingite, serpentine or basaltic rocks are also vein type.

EXPERIMENTS

For the stable isotopic analyses, calcite and dolomite were monominerally separated and reacted with conc-phosphoric acid at 25°C in vacuo. We employed the correction factor for the oxygen in carbonate minerals in this reaction by Hoefs (1987), which was originally based on that of Sharma & Clayton (1964). Magnesite hardly reacted with conc-phosphoric acid at 25°C, therefore, we used an elevated temperature of 90°C. We employed the temperature fractionation factors of

Nagai & Wada (1993) based on Cornides & Kusakabe (1977). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were represented by conventional δ -notation in PDB and SMOW scales, respectively. The mass spectrometer used was a Varian Mat CH-7 at the Department of Earth Sciences, Nagoya University.

ISOTOPIC RESULTS

Isotopic results were shown in Table 1 and Fig. 1. Five magnesite analyses from the quartz-magnesite rock plot in a small range on the carbon and oxygen diagram. Magnesite analyses from the serpentine-magnesite and talc-magnesite rocks also plot in a similar range. Three calcites collected from limestones in the Setogawa Group have a range of carbon and oxygen isotopic composition typical of marine limestone (Hoefs 1987). Other dolomites and calcites analyzed from various carbonated rocks around the Kimitake-zawa plot in a wide range, with $\delta^{13}\text{C}$ values from +1 to -22, and $\delta^{18}\text{O}$ values from +12 to +21.

DISCUSSIONS

In the Kimitake-zawa magnesite deposits, carbonate mineralogy in serpentine-, talc- and quartz-bearing rocks is monomineralic. According to

Table 2 Sample description and carbon and oxygen isotopic values of calcites which filled in veins and in the fractures around the Kimitake-zawa magnesite deposits, Setogawa Group.

Sample No.	Descriptions	$\delta^{13}\text{C(PDB)}$	$\delta^{18}\text{O(SMOW)}$
7071301a	amygdaloidal calcite in camptonite	-15.87	19.80
69no003	amygdaloidal calcite in alkali basalt	-15.84	18.50
7071503	amygdaloidal calcite in alkali basalt	-11.09	14.97
69no58	calcareous tuff	-15.44	17.76
691101tb	calcareous tuff	-13.28	15.87
7152702	secondary calcite in altered basalt	-0.91	19.65
70717510m	interstitial calcite in rodingite	-6.66	15.26
7071807a	interstitial calcite in rodingite	1.33	19.77
704hiro01	ophicalcite	1.56	21.13
704hiri02	ophicalcite	-0.56	19.92
7152501hb	interstitial calcite in actinolite-prehnite rock	-0.65	17.07
7152501pr	prehnite-calcite vein in actinolite-prehnite rock	-5.32	26.59
69111409	calcite in serpentine-calcite rock, composed of fracture zone	-11.49	12.55
7081704	serpentine-calcite-tremolite rock	-20.76	15.22
7081704v	calcite vein in serpentine-calcite-tremolite rock	-19.07	17.21
7091010	calcite-talc-chlorite rock(soapstone?)	-16.28	12.82
701215ls01	calcareous shale	0.40	23.87
701215ls02	limestone	0.47	21.13

Ohashi (1982), carbonates from the basic tuff and black shale consist of calcite-dolomite-magnesite. A formation temperature of 350-400 °C or more could be estimated from the calcite-dolomite solvus with the iron correction from Bickle & Powell (1977) and Goldsmith & Newton (1969).

Both the carbon and oxygen isotopic values of magnesites from the serpentine-, talc- and quartz-magnesite rocks are identical. Although some isotopic values of dolomites plot in the range of magnesite, the carbon isotopic ratios cover a wide range. As previously noted, dolomite occurs as veins cutting magnesite and other host rocks, and was also formed in a later stage of the carbonatization process in this area. Because calcites display such a wide range of isotopic values, especially for carbon, the source of carbon of the calcite must be different from that of magnesite deposits.

In the circum-Izu Massif Serpentine belt, a large scale of magnesite deposits are found only in the Setogawa group. In the older accretional terrain of Sanbagawa metamorphic belt, small scale magnesite veins (up to a few meters in width) were reported by Ito (1983). Miyakawa (1982) reported a large scale magnesite deposits in the Hida marginal belt of Kuzuryu river area. Such carbonated serpentinites will provide an important key to resolve the origin of serpentinite in these tectonic zones.

The origin of the magnesite that occurs with

serpentinite may be a result of the hydrothermal process in the accretionary prism.

ORIGIN OF CARBON IN MAGNESITE DEPOSITS

Recent Ocean Drilling Program results and submersible dives to the inner trench arc high region in front of the Mariana (Fryer 1991) and the Izu-Bonin arcs (Fujioka *et al.* 1993), have revealed that many serpentine diapirs are found at 20 to 40 km from the trench axis. In the Mariana forearc high, some cold carbonate chimneys are found. The carbonate minerals are from a rare hydroxyl hydrate family, the sjogrenite group, and there was no magnesite and dolomite (Fryer 1992). Sakai *et al.* (1990) reported that the hydration of peridotite in the mantle wedge was caused by the fluid squeezed from the subducted slab. The fluid may be involved during the serpentinization and consist mainly of water. Some carbon might be included, but the amount of carbon subjected to carbonatization is less than in the Mariana and Izu-bonin arcs. As pointed out in the previous section, in the circum-Izu massif serpentine belt, such extensively carbonated serpentine bodies are very limited. It is plausible to imagine that some vein calcite and dolomite found in the shale and basalt tectonic breccia in the Kimitake-zawa area is of similar origin to the carbonate vein found in the Mariana arc (Fryer 1992) and Izu-Bonin seamounts (Fujioka *et al.*

1993).

The large scale of carbonatization of the magnesite deposits found in the Setogawa area needs an extra source of carbon species. As seen from carbon and oxygen stable isotope values, $\delta^{13}\text{C}$ values of magnesite deposits indicate that highly homogeneous source materials were necessary to form the deposits. The $\delta^{13}\text{C}$ values of -4‰ (PDB) corresponds to a magmatic source of carbon slightly higher than that of the typical mantle source carbon, represented by carbonatites value of -9 to -5 ‰ (PDB) (compiled by Nelson *et al.* 1988). There is disagreement whether the isotopic values of mantle carbon are inherently homogeneous or include heterogeneities due to mixing of primordial and recycled carbon through subduction during Earth history (Nelson *et al.* 1988). Subducted slabs are cold oceanic plate consisting of oceanic basalts and overlying sediments. The heat source for serpentinization is thought to come from heat flow in deep crustal and mantle sources. It is plausible to imagine that the subduction of an active oceanic volcano or active ridge could supply the heat and carbonate necessary to form massive magnesite-deposits. The origin of carbon in these magnesite deposits is considered to have been derived mainly from a magmatic source together with mixing with normal marine limestone in the region surrounding the serpentine diapirs. As shown in Jedrysek & Halas (1990) and Fallick *et al.* (1991), carbon and oxygen isotopic ratios in small veins in ophiolites and serpentinites show a wide spectrum of values especially for carbon. In this context, carbonate species in fluid that effected the carbonatization of the serpentinite contained various sources of carbon, e.g., marine carbonate and CO_2 derived from organic degradation during diagenesis. The amounts of such carbonates are small. Therefore, the subducting slab may provide some of the carbonate species in a dewatering fluid and small amounts of carbonates will precipitate in the serpentinite sequences as veins.

The chronological frameworks of the formation of the magnesite deposit, and its magmatic characteristics, needs further study with other trace elementary and isotopic analyses such as Sr.

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